NO_2 Sensing Properties of FET Device Attached with $NaNO_2$-based Binary Auxiliary Phase

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As a typical air pollutant that causes photochemical smog and acid rain, Nitrogen dioxide (NO_2) is an urgent target of sensory detection for the sake of air quality control. Various solid-state NO_2 sensors have so far been proposed, such as those using semiconducting metal oxides, solid electrolytes, organic material and SAW devices. Recently we reported a new type NO_2 sensor for which an FET device was coated with $NaNO_2$ over the gate region [1]. Its response to NO_2 was linear to the logarithm of NO_2 concentration at 150°C, but unfortunately its lower detection limit (LDL) for NO_2 was about 200 ppb, far above the environmental standard of NO_2 (40 - 60 ppb) in Japan. In this presentation, the $NaNO_2$ auxiliary phase was modified with $Ca_3(PO_4)_2$ or WO_3 in an attempt to decrease the LDL. The modified FET sensors were found to have the LDL much improved and one of them could detect NO_2 as low as 10 ppb at 130°C.

A schematic drawing of the NO_2 sensor device is shown in Fig.1. A Ta_2O_5 insulation layer was deposited on a commercial FET device by using RF sputtering. A gate electrode (gold) was formed on the surface of Ta_2O_5 outside the usual gate area (70 x 330 μm^2) by using RF sputtering, as shown. The auxiliary material composite, $NaNO_2$-$Ca_3(PO_4)_2$ or $NaNO_2$-WO_3, was mixed well together before hand by melting (300°C) and quenching followed by grinding. A small quantity of the pulverized composite was placed on top of the device to cover the Au gate electrode and Ta_2O_5–layer of the device to be deposited there by a melting-and-quenching method. Gas sensing properties were tested in a conventional gas flow apparatus in the temperature range of 130 - 180°C. Sample gases were prepared by diluting a parent gas of NO_2-air mixture with synthetic air (O_2-N_2).

Figure 2 shows the V_{GS} response of the device attached with $NaNO_2$-$Ca_3(PO_4)_2$ (12:1 in molar ratio) to NO_2 in air at 150°C. The response increased linearly with an increase in the logarithm of NO_2 concentration in the range from 30 ppb to 1 ppm. The slope, 101.4 mV/decade, nominally corresponds to n = 0.9 where n is the number of reaction electron involved in the reduction of NO_2. The LDL of this device was about 30 ppb NO_2 at 150°C, to be compared to about 200 ppb NO_2 of the unmodified device.

The FET device coated with $NaNO_2$-WO_3 (5:1) showed almost the same NO_2 sensing properties as the $NaNO_2$-$Ca_3(PO_4)_2$-coated device at 150°C. However, this device was quicker in response transients, allowing at a lower operation temperature (130°C). At this temperature, the LDL could be extended to 10 ppb as shown in Fig. 3. The Nernst slope in this case was 78.9 mV/decade, which nominally corresponds to n = 1.0. The time of 90% response and recovery to 10 ppb for this device were ca. 5 min and ca. 15 min at 130°C, respectively.

With such features, this type device would be worthy of being investigated in more detail as a promising candidate of the environmental NO_2 sensor.

[1] S. Nakata, K. Shimanoe, N. Miura, N. Yamazoe, Sensors and Actuators B, in press.

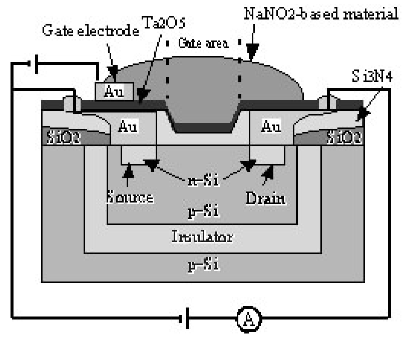

Fig. 1 Schematic drawing of MISFET based NO_2 sensor.

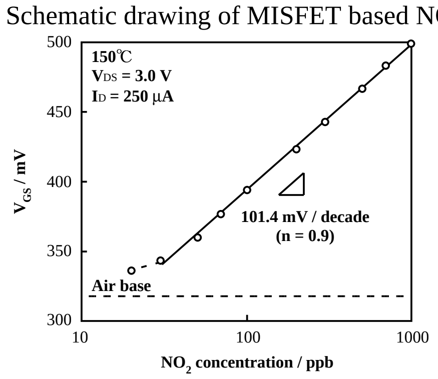

Fig.2 V_G response of $NaNO_2$-$Ca_3(PO_4)_2$ (12:1) attached FET to various concentrations of NO_2 in air at 150℃.

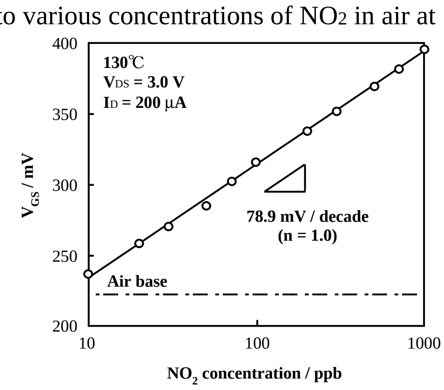

Fig. 3 V_{GS} response of $NaNO_2$-WO_3 (5:1) attached FET to various concentrations of NO_2 in air at 130℃.